Modernizing Methods for Chemical Analysis of Lithium Aluminate Ceramics

The Department of Energy has selected light water reactor irradiation of Tritium Producing Burnable Absorber Rods (TBPARs) as its preferred option for tritium production over the next 40 years. The TPBAR assemblies consist of columns of ^{6}Li-enriched lithium aluminate ceramic pellets that serve a dual purpose of generating tritium and maintaining criticality in the reactor core. A very important aspect of fabricating the assemblies is assuring that the chemical composition and impurity levels of the ceramic pellets are within specified values. Consequently, reliable methods for the chemical analysis of lithium aluminate are required for the program.

The Analytical Chemistry Laboratory (ACL) in CMT first established analytical methods for lithium aluminate when this material was developed at Argonne around 1980 for fuel-cell components and provided analytical chemistry data to DOE contractors when ^{6}Li-enriched ceramics were subsequently being developed as tritium targets. In 1997, ACL provided analysis support to the Tritium Target Qualification Project (TTQP) at Pacific Northwest National Laboratory, which is assisting DOE in developing systems and capabilities for production-scale manufacture of TPBAR assemblies. We analyzed developmental ceramics and later carried out production lot analyses for a demonstration assembly after a multi-laboratory evaluation exercise failed to identify any other laboratories with acceptable capabilities for determining the major constituents (Li and Al).

The methods currently in place are laborious, time-consuming, and require special apparatus or skills not readily available in private-sector laboratories. To lower cost, enhance throughput, and allow commercial availability of analytical chemistry for the TPBAR ceramics, we have been investigating alternative methods to replace the wet-chemical methods previously used. One new method developed for dissolving the ceramic involves a microwave-accelerated acid dissolution that exploits recently available commercial technology (see figure below). A new method being employed for determining Li and Al content is based on inductively coupled plasma-optical emission spectrometry (ICP-OES) and was adopted from the National Institute of Standards and Technology (NIST). Efficient methods for measuring impurities such as carbon, halides, and metals have also been developed.

MARS-5 Microwave System
(CEM Corp., Matthews, SC)

Performance of the microwave method was tested by filtering solutions from several ceramics having different process histories and weighing the residues. Filters were 0.2-micron polycarbonate membranes. The method averaged 99.98% dissolution and met our goal of >99.9%. We also met the analytical goals for major constituents and impurities (see tables on next page).

Efforts are in progress to transfer our new methods to commercial laboratories contracted by the TTQP. Meanwhile, we are using the methods to provide analysis support to ceramic manufacturers developing production-scale techniques for pellet fabrication and to characterize materials DOE intends to use for laboratory quality control during the production decades. The investment made by DOE to modernize the methods available for analyzing lithium aluminate will return substantial dividends over the program's life.

ANL Participants

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Required Precision and Allowed Bias in Analysis of TPBAR Assemblies for Major Constituents and Impurities

	Measured	Precision, %RSD	Allowed Bias, %
Li Isotopes	6/7 Ratio	0.45	0.40
Li Assay	wt% Li	0.45	0.40
Al Assay	wt% Al	0.45	0.40
Carbon	wt% C	20	25
Halides	F, Cl, Br, I	20	25
Cations & Neutron Poisons	23 Metals	20	25

Results summary from Li and Al assays of five samples with ICP-OES. The pooled relative standard deviations (precision) are 0.06% for Li and 0.02% for Al. The average percent differences (allowed bias) are -0.03% for Li and -0.06% for Al. These results greatly exceed the goals specified in the above table.

Sample No.	**1**	**2**	**3**	**4**	**5**
at.% ^{6}Li	7.5	20	30	40	95
Li Assay RSD, %	0.07	0.08	0.04	0.06	0.05
% Diff. from Known	-0.04	-0.09	-0.08	-0.10	+0.07
Al Assay RSD, %	0.01	0.02	0.02	0.03	0.03
%Diff. from Known	-0.03	-0.06	-0.08	-0.10	-0.01